Review of Techno-Economic Analysis Studies Using Physical Solvents for Pre-Combustion CO₂ Capture

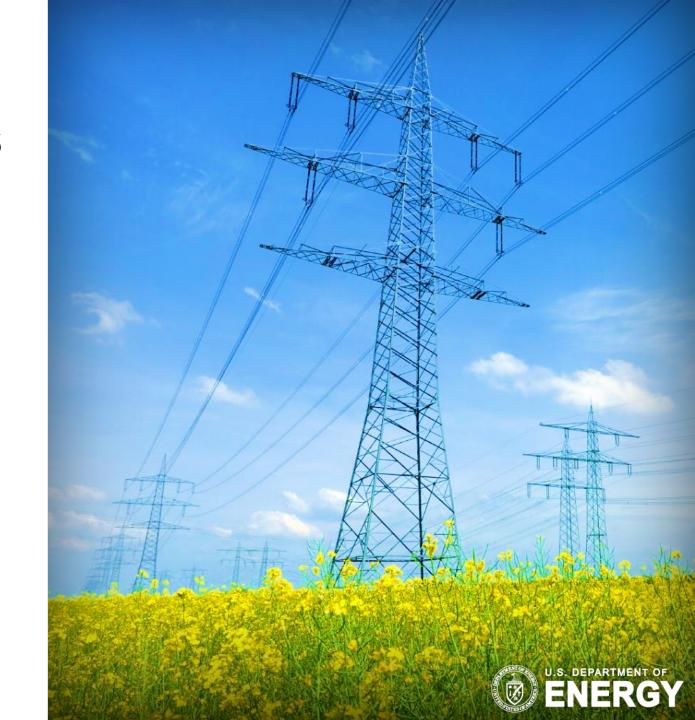
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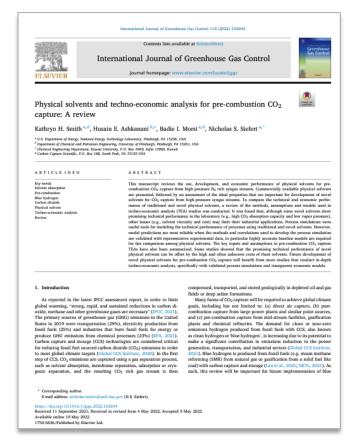




Overview



- Introduction to pre-combustion carbon capture
 - Applications & technology options
- Physical solvents for CO₂ capture
 - Commercial solvents
 - Ideal properties for development of new solvents
 - Novel solvents
 - Outlook for future development
- Techno-economic analysis (TEA) of pre-combustion CO₂ capture using physical solvents
 - Process model
 - Economic model
 - TEA outcomes, limitations and future development
- Recommendations for future development of novel physical solvent absorption processes for pre-combustion CO₂ capture



Smith, K.H., Ashkanani, H.E., Morsi, B.I., Siefert, N.S., 2022. Physical solvents and techno-economic analysis for pre-combustion ${\rm CO_2}$ capture: A review. International Journal of Greenhouse Gas Control 118. <u>Link</u>



Pre-Combustion Carbon Capture

- Pre-combustion carbon capture is when CO₂ is captured from a fuel gas before it is combusted in a gas turbine to produce electricity or before it is used as a feedstock in another application
- Examples of pre-combustion CO₂ capture include:
 - Pre-combustion CO₂ capture at IGCC power plants
 - Production of clean (blue) H₂ from gasification and natural gas reforming processes
 - Adjustment of CO/H₂ composition for coal & biomass to liquids
 - Removal of CO₂ from syngas for chemical/fuel production (e.g. ammonia/fertilizer)
- Technology options for CO₂ capture:
 - Solvents
 - Membranes
 - Sorbents
 - Integrated & hybrid options



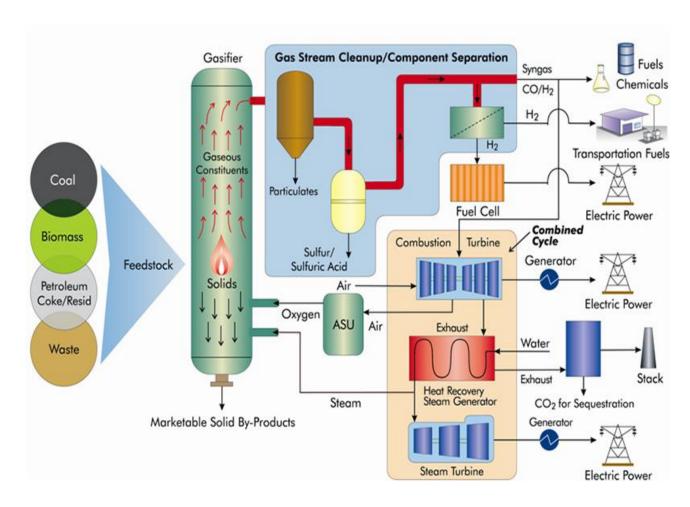


Figure 1. Gasification applications



Commercial Physical Solvents for CO₂ Capture



Commercial physical solvent processes

Selexol (DEPG)

Rectisol (Methanol)

Purisol (NMP)

Others
(e.g. propylene carbonate)

ADVANTAGES

- Hydrophilic solvents
- Commercially available at large scale
- Inexpensive
- High CO₂ absorption capacity
- High selectivity for CO₂ & H₂S over other syngas components
- Low vapor pressure (Selexol)

CHALLENGES

- Energy intensive due to low temperature operation
- High viscosity at low temperature (reduces mass transfer performance)
- Water absorption
- High vapor pressure (Rectisol)

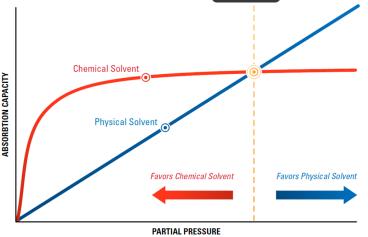


Figure 2. Physical & Chemical Solvents

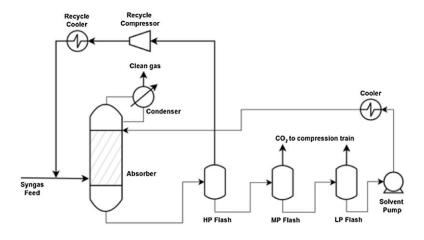


Figure 3. Typical physical solvent absorption flow diagram



Novel Physical Solvents for CO₂ Capture



Ideal properties of physical solvents

- High CO₂ capacity
- Favorable selectivity for CO₂ over other fuel gas components, including CH₄, H₂, N₂ & CO
- Low vapor pressure
- Non-foaming
- Low water uptake
- High CO₂ diffusivity
- High thermal stability
- Low cost
- Low toxicity
- Simple solvent synthesis
- Environmentally benign

Novel physical solvents

Ionic Liquids

- Many imidazolium based ILs including [bmim][PF₆], [bmim][BF₄], [hmim][Tf₂N], [bmim][Br]
- Hydrophobic IL [aPy][Tf₂N]

Hydrophobic solvents

 Examples include TBP, PDMS, PPGDME, PEG-PDMS-3, CASSH-1

Others

eg. Deep eutectic solvents

NIST 27,000 compounds

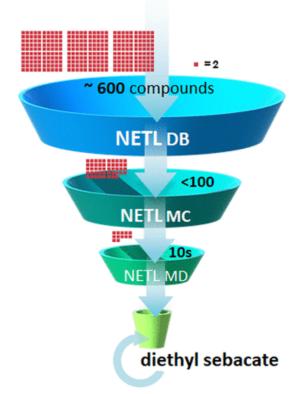


Figure 4. Schematic of a computational scheme used to screen physical solvents for CO₂ pre-combustion capture



Literature assessment of physical solvents for CO_2 capture N_2



Bench scale experiments

- Solvent physical properties, CO₂ solubility, gas selectivity, etc.
- Some physical solvents, such as ILs, show high CO₂ solubility and low vapor pressure but can have high viscosity and high synthesis costs
- Hydrophobic solvents have the benefit of not absorbing water, but can have issues with selectivity (e.g. PDMS), formation of gels (eg. PPGDME) or foaming (e.g. PEG-PDMS-1)

Process simulations



- Optimize the technical performance of physical solvents
- Need to be validated with representative experimental data

• Techno-Economic Analysis (TEA) studies 🕅

- Limited comprehensive TEAs and performance baselines for pre-combustion carbon capture using physical solvents
 - Technical performance: CO₂ solubility, selectivity, viscosity, heat capacity, process optimization, etc
 - Economic performance: CAPEX, OPEX, etc

For more information see literature review manuscript:

Smith, K.H., Ashkanani, H.E., Morsi, B.I., Siefert, N.S., 2022. Physical solvents and techno-economic analysis for pre-combustion CO₂ capture: A review. International Journal of Greenhouse Gas Control 118.

<u>Link</u>

Solvent	[hmim][Tf ₂ N]	[aPy][Tf ₂ N]	Diethyl sebacate (CASSH- 1)	PEG-PDMS-3 (or disub-4PEG)	Tributyl phosphate (TBP)		
Solvent type	Ionic liquid	Ionic liquid	Hydrophobic solvent	Hydrophobic solvent			
Molecular formula	$C_{12}H_{19}N_3F_6O_4S_2$	$C_{10}H_{10}N_2S_2O_4F_6$	$C_{14}H_{26}O_4$	$C_{26}H_{60}O_{10}Si_3$	$C_{12}H_{27}O_4P$		
Chemical structure	her al	* ~	~!~~~~	broom XX			
Molecular Weight kg/kmol	447	399	258	620	266		
Viscosity @ 25°C (cP)	71	28	5.1	12.2	2.9		
Density @ 25 °C (kg/m ³)	1371	1507	960	987	979		
Vapor pressure @ 25 °C (Pa)	small	< 0.09	0.0012	small	0.15		
Melting point (°C)	- 3 ± - 2		5	-	- 80		
Boiling point (°C)	635		312	high	289		
Thermal conductivity @ 25°C (W/ m•K)	0.12	0.23	0.15	0.17	-		
Specific heat @ 25°C (J/g•K)	1.41	1.11	-	-	1.426		
CO ₂ Henry's Law constant @ 25°C (mol/(MPa.L))	~0.8	~1.1	~1.3	~1.2	1.1*		
CO ₂ /H ₂ selectivity @ 25 °C	~30	~100	66	58	61*		



Techno economic analysis of CO_2 capture using physical solvents N

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<u>Technical performance – Process simulation</u>

- Multiple process simulation tools available
 - e.g. Aspen Plus, Aspen HYSYS, ProTreat, etc.
- Define process boundaries & technical assumptions
- Optimize process based on specific design target
 - CO₂ capture rate, product pressure, etc
- Obtain equipment sizes and energy demands
 - Important for accurate estimation of economics
- Consider model assumptions and validation of correlations used to predict process performance
 - Several EOS models (eg. SRK-EOS, PC-SAFT,...) available for predicting VLE and mass transfer performance
 - Need accurate models for predicting physical properties

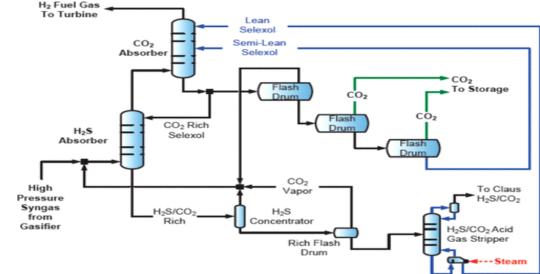


Figure 5. Dual stage Selexol process flow diagram

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Reference	Solvents	Gasification type and/or syngas composition details	Gas flow rate, kg/s	Gas flux, kg/s/ m ²	Gas Pressure, bar	Gas Temp.° C	Solvent Flow rate, kg/s	Liquid Flux, kg/ s/m ²	L/G	Solvent Temp. °C	Absorber Diameter, m	Absorber height, m	Physical property model	Process simulator	CO ₂ capture rate, %	Flash pressure HP/MP/LP, bar	CO ₂ compressi specificati
Dave et al. (2016)	Selexol	307 MWe Syngas: 42.3% CO ₂ , 46.6% H ₂	163	5.1	37	26	1,604	50	10	20	6.4	16	PR-EOS	ProTreat v5.2 2013	90	35.2	n/a
Basha et al. (2013)	[hmim] [Tf ₂ N]	400 MWe E-Gas with Pitt. Coal #8, 23.9% CO ₂ , 37.5% H ₂	25.6*	5.7	30	227	1,038	229	40	24.9	2.4*	30°	PR-EOS & Span-Wager EOS	Aspen Plus	97.3	20/10/1	153 bar 260 K
Basha et al. (2014)	TEGO IL K5 TEGO IL P51P	400 MWe E-Gas with Pitt. Coal #8, 23.9% CO ₂ , 37.5% H ₂	25.6*	1.6	30	227	900 250	57 16	10- 35	24.9	4.5*	27*	PR-EOS & Span-Wager EOS	Aspen Plus v7.2	92	20/10/1	153 bar 260 K
Siefert et al. (2016a)	Selexol PEG- Siloxane1 IL – [aPy] [Tf ₂ N]	464 MW GEE gasifier, 40.3% CO ₂ , 56.3% $\rm H_2$	147	4.4	52	40	1,514- 3,154	46-74	10- 17	10-40	6.5	36	PC-SAFT	Aspen Plus	90	20.7/11/ 1.5	15 MPa 323 K
Field and Brasington (2011)	Selexol (DEPG)	464 MW GEE gasifier, 40% CO ₂ , 56% H ₂	227	n/a	52	17	1,939	n/a	8.5	10	n/a	n/a	PC-SAFT	Aspen Plus v7.1	90	20.7/11/ 1.5	153 bar 50 °C
Park et al. (2015)	Selexol (DEPG) Rectisol (MeOH) Purisol (NMP)	Udhe entrained flow coal gasifier	n/a	n/a	37	0	95 7.3 145	35 1 24	n/a	-10 -20 to -40	1.87 3 2.8	25 28 28	PC-SAFT	Aspen Plus v7.3	90	3 stage LP/ MP/HP	n/a
Zhai and Rubin (2018)	[hmim] [Tf2N]	Shell gasifier, 41% CO _{2,} 59% H ₂	-78 ⁺	n/a	29.6	29	2,439	n/a	-30	29.4	n/a	n/a	modified RK EOS	IECM v9.5	90	3 stages 10 to 0.8 bar	153 bar

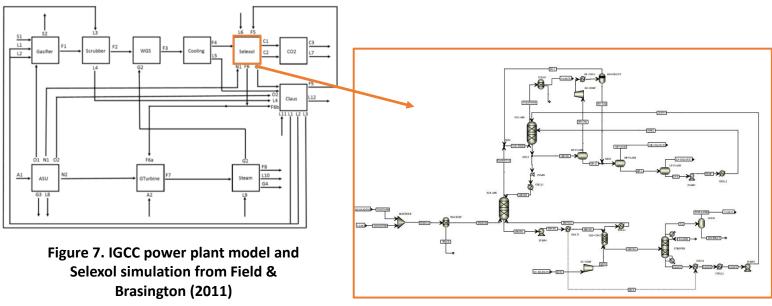


TEA of CO₂ capture using Selexol process

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Selexol process simulation

- Field & Brasington (2011) developed a comprehensive & freely available model for an IGCC power plant with CO₂ capture using Selexol (Aspen Plus).
- This baseline model provides a transparent and consistent framework for analyzing IGCC flowsheets and process innovations.
- Selexol was represented as single DEPG component with VLE predicted using the PC-SAFT EOS & regressed binary interaction parameters at 25°C (temperature dependent data was not available).



Experimental viscosity data from Li et al. 2007 & NETL

10

25°C exp.
30°C exp.
40°C exp.
50°C exp.
60°C exp.
70°C exp.
A NETL lab 25°C
25°C Aspen
30°C Aspen
50°C Aspen
60°C Aspen
60°C Aspen
60°C Aspen

Figure 8. Viscosity of Selexol/water mixtures and Aspen Plus prediction.

Selexol (Gensorb 1753) mass fraction

- PC-SAFT EOS in Aspen Plus is not suitable for predicting viscosity of Selexol with increasing water absorption (see Fig.8).
- Aspen Plus predictions for CO₂ uptake, at defined temperature
 & pressure, can be lower than experimental values.
- Aspen Plus predicted dependence of H₂ uptake with temperature is opposite to that seen in experimental studies

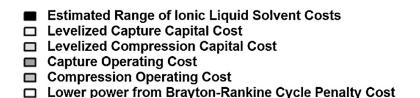


TEA of CO₂ capture using physical solvents

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Economic performance

- Estimate capital costs (CAPEX) & operating costs (OPEX) of process using cost equations/correlations and relevant values/assumptions for:
 - Electricity cost
 - Capacity factors
 - Plant life
 - Construction time
 - Operating and maintenance costs
 - CO₂ capture rate
 - Inflation/discount rates
 - Solvent cost
 - Currency conversion
 - Location factors
- All assumptions should be transparent and realistic
- Consider system boundaries and assumptions when comparing levelized cost of capture (LCOC) or levelized cost of electricity (LCOE) etc. between different processes
- Sensitivity analysis around economic assumptions can be useful
 - E.g. CO₂ removal efficiency, solvent costs, etc.



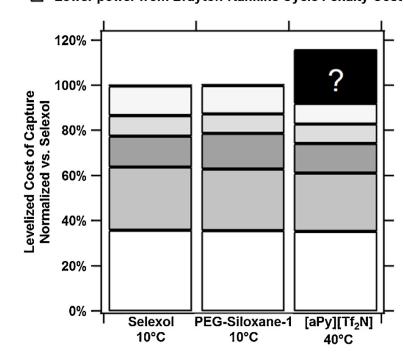


Figure 9. LCOC for three physical solvents. Solvent cost can have a big impact on the overall cost or LCOC.

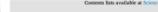


Some highlights from assessing TEA studies for pre-combustion CO₂ capture using physical solvents



- When comparing results from different TEA studies be cautious of process scales and boundaries does the TEA/process include water gas shift, CO₂ compression, H₂S removal, etc.? (Smith et al. 2022)
- Consider plant-wide cost reductions (eg. compression technology) as cost of CO₂ capture accounts for less than 10% of IGCC plants total capital investment (Zhai & Rubin, 2018)
- Different mass transfer coefficient correlations from Aspen Plus were found to impact the capture costs of the Selexol process from \$27 to \$31/ton CO₂ (Xin et al. 2020)
- For solvent plant only, the majority of LCOC is independent of solvent used. However, the cost to synthesize a solvent at commercial scale can be important, particularly for novel solvents like ionic liquids (Siefert et al. 2019)
- Solvent physical properties like viscosity and heat capacity can have a strong impact on total annualized cost for some ILs with high viscosity the cost of heat exchangers were two orders of magnitude higher than the absorber cost (Mota-Martinez et al. 2018)
- CO₂ removal efficiency target will impact cost with a number of studies finding 90% CO₂ removal providing lowest CO₂ avoidance cost (Chen and Rubin, 2009).
- Low absorber operating temperature and non-corrosive solvents were found to provide low LCOC due to smaller absorption columns, lower solvent flow rates and use of less expensive materials of construction (Ashkanani et al. 2019)
- Integrating CO₂ capture at an IGCC plant can a have a wide variation in cost of CO₂ avoided (30-86 \$/t CO₂) due to different assumptions and methodologies used in economic analysis (e.g. inclusion or exclusion of inflation rate, contingencies, etc.) (Jansen et al. 2015)







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Physical solvents and techno-economic analysis for pre-combustion CO₂ capture: A review

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ARTICLEINFO

Rey words: Solvent absorption Pre-combustion Blue hydrogen Carbon dioxide Physical solvent

This manuscript revises the use, development, and economic performance of physical solvents for precombustation Go, garpense from high personnel by city support streams. Commercially available physical solvents are presented, fellowed by an assessment of the ideal proportion that are important for development of zerols solvents for Go, capture from high-personnel systems. To compare the technical and recommitment of traditional and movel physical subvents, a review of the methods, assumptions and models used in techno-economic analysis (TLM) statistics was candiscribt. It was found that, affixing them movel associated to techno-economic analysis (TLM) statistics was candiscribt. It was found that, affixingle seem most indevents show under losses (e.g., solvent viscosity and cost) any limit their industrial applications. Process simulations were useful took for modeling the technical performance of processes using traditional and more adverse. Becover, model predictions are most reliable when the methods and correlations used to develop the process simulations were availabled with representative experimental data, in particular highly accurate baseline models are required for fair comparison among physical solvents. The key inputs and assumptions in pro-combustion CO₂ capture TLM have also been summarized. Some studies showed that the promising technical performance of zovel TLM have also been summarized. Some studies also that the promising technical performance of zovel techno-economic analysis, sucrelifically with validated presses simulations and transserrant exceeds models.

1. Introduction

As reported in the latest IPCC assessment report, in order to limit global warming, "strong, rapid, and sustained reductions in carbon dioxide, methane and other greenhouse gases are necessary (IPCC, 2021). The primary sources of greenhouse gas (GHO) emissions in the United States in 2019 were transportation (2019a), electricity production from feasif luck (25%) and industries that burn fossil fuels for energy or produce GHG emissions from chemical processes (2943) (EPA 2021). Carbon capture and storage (CCS) technologies are considered critical for reducing lossifies that source dearth officed for reducing lossifies that source dearth officed for reducing lossifies that source dearth officed for the consideration of the control of

compressed, transported, and stored geologically in depleted oil and gas fields or deep saline formations.

Many forms of CO₂ capture will be required to achieve global climate goals, including but not limited to (a) direct air capture, (b) post-combustion capture from large power plants and similar point sources, and (c) per-combustion capture from mid-tream facilities, gastification plants and chemical refineries. The demand for clean or near-zero emissions hydrogen produced from fossil fache with CO₃ also known as clean hydrogen or "blue hydrogen," is increasing due to its potential to make a significant contribution to emissions reduction in the power generation, transportation, and industrial sectors (Goldoni CCI Instriate, 2021). Blue hydrogen is produced from fossil flesh (e.g. steam methane reforming (SMR) from natural gas or gastification from a solid fate like coally with carbon capture and storage (Lau et al., 2021; NETI, 2021). As such, this review will be important for future implementation of blue

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More information & references can be found in IJGGC review paper:

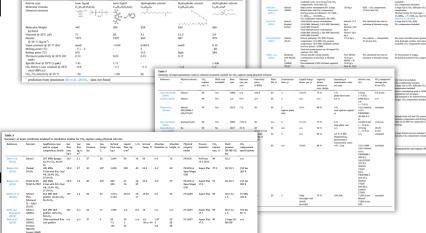


Conclusions



- Physical solvents can be used for pre-combustion carbon capture and CO₂ removal from syngas for other gasification applications
- Novel physical solvents (e.g. Ionic liquids, hydrophobic physical solvents, etc.) show promising technical performance
 - High CO₂ absorption capacity
 - Low water absorption
 - Low vapor pressure
- Need to consider both technical and economical performance of novel solvents
 - Solvent physical properties and costs are also important
- Techno Economic Analysis studies are useful tools when assumptions and methodologies are comprehensive and transparent
 - Model predictions should be validated with experimental data
 - Assumptions, scale, operating conditions and process boundaries should be clearly defined in process model
 - Key inputs and assumptions for economic models should be listed
- More accurate baseline models are required for fair comparison between novel processes







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